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(21) International Application Number: PCT/SE93/00868 (22) International Filing Date: 25 October 1993 (25.10.93) (30) Priority data: 9203122-8 26 October 1992 (26.10.92) SE (71) Applicant (for all designated States except US): SCA-WIFS-TA-ÖSTRAND AB [SE/SE]; P.O. Box 123, S-861 00 Timrå (SE). (72) Inventors; and (75) Inventors/Applicants (for US only) : ANNERGREN, Göran [SE/SE]; Granbacken 14, S-856 34 Sundsvall (SE). LUNDIN, Maria [SE/SE]; Hagevägen 22 A, S-856 41 Sundsvall (SE). (74) Agents: GRAUDUMS, Valdis et al.; Albihn West AB, P.O. Box 142, S-410 22 Göteborg (SE).		(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>In English translation (filed in Swedish).</i>
(54) Title: METHOD FOR PEROXIDE BLEACHING OF SULPHATE PULP (57) Abstract <p>The invention relates to a process for peroxide bleaching of sulphate cellulose which has been prebleached in an acid oxidative step and thereafter washed. During the last washing or in a last separate step before the peroxide addition, magnesium is added in an amount of 0,1-10 kg magnesium per ton pulp, preferably more than 2 kg per ton pulp.</p>		

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5 **TITLE:**

Method for peroxide bleaching of sulphate pulp.

TECHNICAL FIELD:

10 The present invention relates to a process for peroxide bleaching of sulphate pulp which has been prebleached in an acidic oxidative step and the invention relates primarily to a pretreatment of the pulp before the addition of peroxide.

15 **PRIOR ART:**

Chlorine, alkali, hypochlorite and chlorine dioxide have been used for bleaching cellulose pulps. During the last 20 years chlorine and hypochlorite have been replaced by oxygen gas, chlorine dioxide and peroxide with the aim to decrease the environmental problems which are believed to be caused by chlorinated organic compounds. The result is that it is nowadays doubtful whether remaining environmental problems can be attributed to chlorinated substances. The opinion that chlorinated compounds are dangerous have, however, resulted in extreme demands on the market to bleach completely without chlorine chemicals, that means also a replacement of chlorine dioxide. To achieve qualified bleaching the chemicals oxygen gas, peroxide and ozone will then be actual. It is, however, doubtful whether these chemicals provide any substantial environmental improvement over pure chlorine dioxide bleaching if the introduction of these chemicals is not combined with external purifying or a very thorough closing of the systems so that the amount of discharged substance to the drainage will be substantially reduced. An important development question is therefore to adapt the bleaching technique so that closing can be facilitated.

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Cellulose pulps are usually produced by boiling wood according to the sulphite or sulphate method and the pulp is further treated in various steps for removing of lignin and other substances so that the pulp gradually becomes brighter and brighter. One of the earlier bleaching steps for i.a. sulphate pulp is carried out by oxygen gas bleaching in an alkaline environment thereof which is usually called oxygen delignifying.

With regard to peroxide bleaching of oxygen delignified sulphate pulp, a process has been developed in which the pulp is pretreated with a complex forming agent at elevated temperature and a pH between 6 and 7 whereupon the pulp is washed and bleached with peroxide, usually without special protecting additions in the peroxide step. The pretreatment is aimed at giving the peroxide step stability, which means that the bleaching becomes selective and without any appreciable degradation of carbohydrates, which is the cellulose. What is very important for this stability is the absence of substantial amounts of transmission metals such as manganese and iron in the pulp and presence of magnesium.

TECHNICAL PROBLEM:

Both the oxygen step and the ozone step are degrading on the carbohydrates, which means that the space for the carbohydrate degradation in the peroxide step will be severely limited. Very good stability is therefore required for peroxide bleaching. For limited bleaching efforts, all reasonable peroxide steps should be stable, which i.a. implies that the decrease of the pulp viscosity with increasing brightness is low. When the bleaching is sharpened, a critical brightness will eventually be obtained above which the viscosity decrease increases dramatically. The more stable the system is, the higher the critical brightness seems to be. An analysis of the

critical brightness should accordingly characterize the stability of the peroxide bleaching.

5 A pretreatment according to the above with a complex forming agent at pH 6 to 7 and high temperature gives in many cases required stability but has the environmental disadvantage that the water from the pretreatment must be removed from the system, thereby making a development of extended closing of the system more difficult and thus
10 gives discharges which contain complex forming agents which, from an environmental point of view, are not desirable. One can also stabilize the system when bleaching mechanical pulp by addition of silicate and a smaller amount of magnesium salt to the peroxide step. The addition
15 of silicate makes, however, the possibility to use the peroxide backwater (by "backwater" is meant the water which after the bleaching is discharged from the system) in the closed system much more difficult in connection with recovery of black liquor for chemical recovery since the
20 tolerances for silicate in the recovering system are very low.

If therefore the peroxide step as an oxidising step comes directly after the oxygen delignifying step and since the
25 above mentioned pretreatment steps must be carried out in a relatively open system, said demand for a substantially positive environmental effect of an appreciable reduction of the discharge of organic substances will hardly be fulfilled.

30 THE SOLUTION:

By means of the present invention, the problems connected with the above said stabilizing processes are solved and a process is provided for peroxide bleaching of sulphate pulp
35 which has been prebleached in an acid oxidative step and thereafter been washed to a lignin content of less than

1,3% and a manganese content of at most 30 ppm, preferably at most 20 ppm which process is characterized in that during the last wash, or in a last separate step for the peroxide addition, magnesium is added at a high pH in an amount of 0,1 to 10 kg Mg^{++} per ton pulp, preferably more than 2 kg per ton pulp during good mixing and up to 1 minute before the addition of peroxide.

According to the invention it is advantageous that magnesium be added in the form of a salt, for example $MgSO_4$ or as an oxide MgO .

The wash can according to the invention suitably be carried out on a filter on a rotating drum, whereby washing liquid is fed consecutively through following nozzles and that the magnesium solution is fed through the last nozzles.

It is also possible to add the magnesium solution as a diluent directly before the peroxide bleaching step.

The magnesium salt or oxide can be dissolved in acid backwater from a later bleaching step in the bleaching process or in a neutral or weakly alkaline backwater from later bleaching steps containing Mg^{++} complex forming backwater substances to prevent M^{2+} precipitating due to a high pH.

As appears from the above, the addition of magnesium can contrary to the earlier discussed pretreatment, be varied within relatively wide limits. The temperature is not critical. As mentioned above, it is also sufficient to have a very short treatment time. The choice of pH influences to some extent the solubility of the magnesium salt as some risk for precipitation exists at high pH.

By means of the wash after the acid oxidative prebleaching step, the pulp obtains a low metal content and the lignin content of the pulp will at the same time be low, less than 1,3%.

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By means of the present invention it has accordingly been shown that it is possible to stabilize the peroxide bleaching to a sufficient extent by only a simple addition of Mg^{2+} so that in a multistep process of for example the type peroxide-ozone-peroxide it is possible to bleach the sulphate pulp (also pinewood sulphate pulp) to full brightness according to traditional standard without too serious degradation of carbohydrates seen as a whole and with very small carbohydrate degradation in the peroxide step. The first peroxide step is thereby expected to give a brightness increase of about 20 units without reaching the critical brightness where the brightness increase is retarded when the degradation of carbohydrates continues with an reduced or even increased speed. The process is primarily suitable for so-called middle concentration (MC) bleaching but it is not limited to this level of the pulp concentration. By middle concentration is meant a concentration of pulp of the order of 10-15% in water.

As mentioned above it can be suitable to add the magnesium at a relatively late stage of the last washing step so that the majority of the magnesium ions will remain in the pulp or in the water which leaves the wash together with the pulp. When pressure washing, or some other wash which allows for dilution after the washing before the pulp is to be bleached in the peroxide step, the addition of magnesium can occur with a dilution liquid after the washing. It is very important that the magnesium ions are homogeneously distributed in the pulp and suitable apparatus for obtaining this must then be used.

An advantage with the present process is that the stabilizing, contrary to stabilizing with a complex former at high temperature and pH 6-7, does not need any special step for treatment but can to a very high degree be integrated in the apparatus for further steps.

The invention will be further described below in connection with the attached diagrams.

Diagram 1 shows the brightness in percentage according to ISO-standard dependent of consumed hydrogen peroxide per ton pulp. The bleaching was carried out in all diagrams at a pulp concentration of 12%. In the diagram, two curves are shown, curve A for non-stabilized pulp and curve B for stabilized pulp.

As appears from the diagram, a substantial increase in the brightness of the magnesium-stabilized pulp was obtained in relation to the non-stabilized pulp at a hydrogen peroxide consumption from 3 kg per ton pulp and more.

Diagram 2 shows further the value of the intrinsic viscosity in relation to consumed hydrogen peroxide per ton pulp. As appears from the diagram, the intrinsic viscosity decreases for the magnesium-stabilized pulp much more slowly than for the non-stabilized pulp, which is an indication that the cellulose has not been degraded to the same extent in the stabilized pulp.

Diagram 3 shows how the brightness increases at increased use of magnesium ions up to a consumption of about 2 kg magnesium per ton pulp, whereupon the curve planes out.

Diagram 4 shows the change in intrinsic viscosity by increased use of magnesium ions in the pulp. In the same way as in connection with the curve of brightness in

5 CLAIMS:

1. Process for peroxide bleaching of sulphate pulp which has been prebleached in an acid oxidative step and thereafter washed to a lignin content of $< 1,3\%$ and an Mn^{++} content of at most 30 ppm, preferably at most 20 ppm, characterized in that during the last wash or in a last separate step before the addition of peroxide, magnesium is added at a high pH in an amount of 0,1-10 kg Mg^{++} per ton pulp, preferably more than 2 kg per ton pulp, under good mixing and up to 1 minute before the peroxide addition.

2. Process according to claim 1, characterized in that the magnesium is added as a salt, for example $MgSO_4$, or as an oxide MgO .

3. Process according to either of claims 1 and 2, whereby the wash is carried out on a filter on a rotating drum where washing liquid is supplied through consecutively following spray nozzles, characterized in that the magnesium solution is added through the last spray nozzles.

4. Process according to either of claims 1 and 2, characterized in that the magnesium solution is added as a dilution liquid immediately before the peroxide bleaching step.

5. Process according to any of claims 1-4, characterized in that the magnesium salt or oxide is dissolved in acid backwater from later bleaching steps in the bleaching process.

diagram 3, the curve rises for the intrinsic viscosity to a consumption of about 2 kg magnesium per ton pulp whereupon the curve planes out.

- 5 The invention is not limited to the shown process but can be varied in different ways within the scope of the claims.

6. Process according to any of claims 1-4,
c h a r a c t e r i z e d i n that magnesium salt or
oxide is dissolved in a neutral or weakly alkaline back-
water from later bleaching steps containing magnesium ions
5 complex forming backwater substances.

7. Process according to any of claims 1-6,
c h a r a c t e r i z e d i n that the temperature at the
Mg⁺⁺ treatment is 20-90°C.

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DIAGRAM 1 1/2

Brightness% ISO

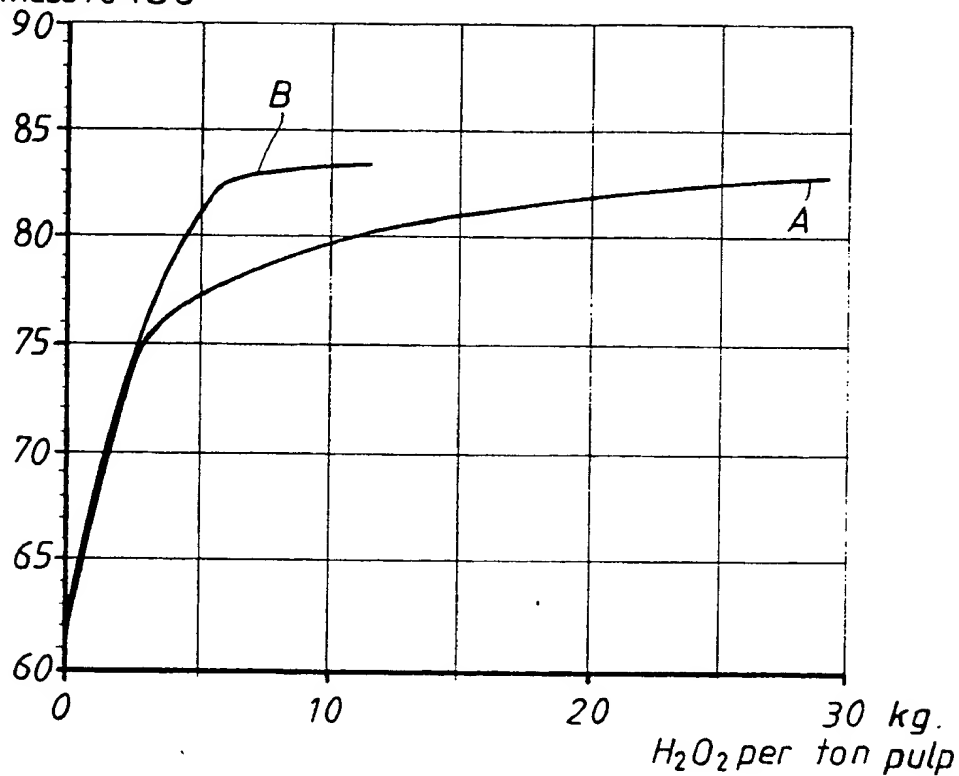
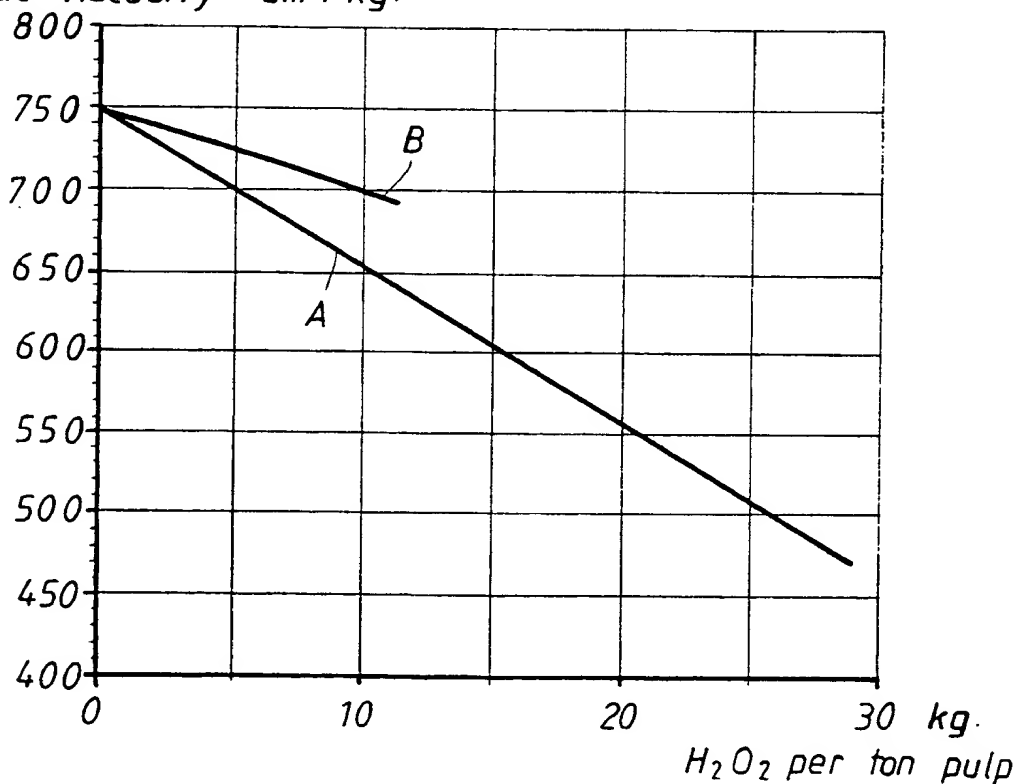
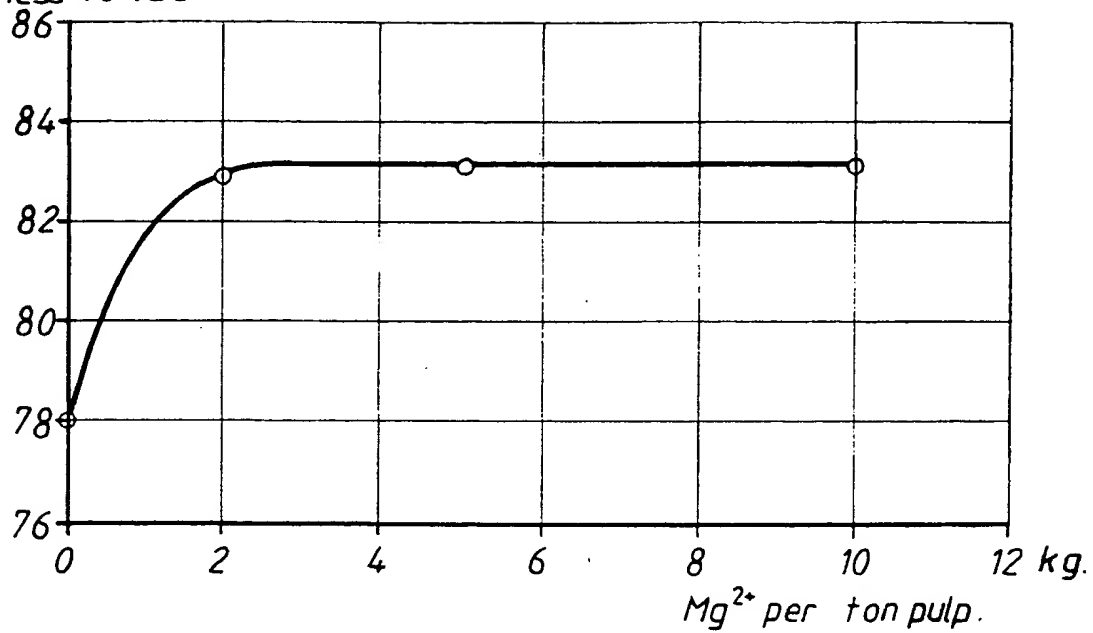
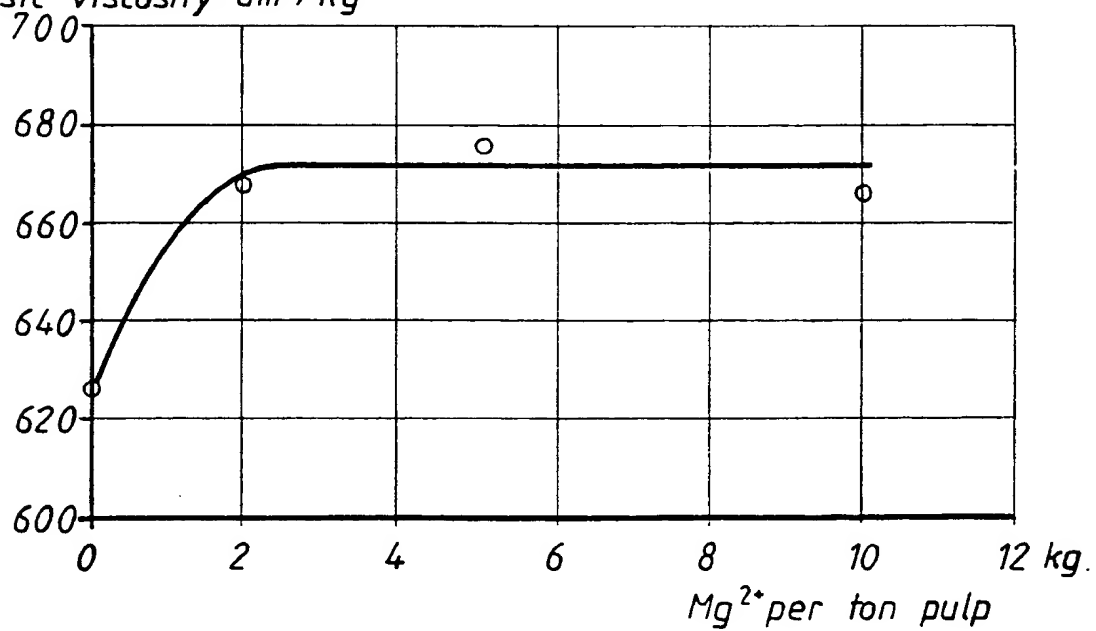


DIAGRAM 2

Intrinsic viscosity $dm^3/kg.$



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DIAGRAM 3*Brightness % ISO*DIAGRAM 4*Intrinsic viscosity dm^3/kg* 

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: D21C 9/10, D21C 9/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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IPC5: D21C

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	EP, A1, 0511695 (EKA NOBEL AB), 4 November 1992 (04.11.92), page 2, line 43 - page 4, line 11 --	1-7
A	DE, C2, 2841013 (DEGUSSA AG), 7 June 1984 (07.06.84), column 3, line 2 - line 16 -- -----	1-7



Further documents are listed in the continuation of Box C.



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